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ORIGINAL RESEARCH

Behaviors of helium in vanadium: Stability, diffusion, vacancy trapping and ideal tensile strength

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Abstract The behaviors of helium in vanadium including stability, diffusion, and its interaction with vacancy as well as its effects on the ideal tensile strength was investigated by a first-principles method. The activation energy barrier of helium was calculated to be 0.09 eV, which is consistent with the experimental result. The results indicated that the vacancy can lead to a directed helium segregation into the vacancy to form a helium cluster since the vacancy provides a "lower atomic and electron density region" as a large driving force for helium binding. It is easy for a mono-vacancy to trap helium and form a He_nV complex. The first-principles computational tensile test demonstrates that helium obviously decreased the tensile strength of vanadium.

1. Introduction

Many investigations have been made on the effects of impurity in metals as well as intermetallics [1–12], which is one of the important issues for metals as the structural materials. Among them, vanadium as well as its-alloys is considered as possible candidates as the structural materials in fusion reactors. Under the irradiation of 14.1 MeV high energy neutrons, helium is produced from the (n, α) transmutation reactions in vanadium and can be easily trapped by the defects such as vacancies [5]. Helium with the low concentration case may potentially cause the materials embrittlement [7], while helium of high concentration can lead to the formation of helium bubbles [7,8]. Consequently, the influence of helium content in vanadium is an important issue and requires more investigation.

Previous experimental observations [13–15] suggested that helium could easily bind with the vacancies. Recent semi-empirical [16] and first-principles studies [5,17,18] showed that

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helium prefers to occupy the tetrahedral interstitial site in bulk vanadium, and two helium atoms in bulk vanadium bonds with each other with an equilibrium distance of 1.68 Å [17] and a binding energy of ~0.30 eV [16]. With the presence of vacancy, the semi-empirical potentials results [16] showed that helium easily binds with the vacancy with the binding energy of ~3.10 eV. Seletskaia et al. studied systematically a single helium in a vacancy of vanadium as well as other metals such as molybdenum, niobium, tantalum, and tungsten [19], and found that helium prefers to be trapped by the vacancy. However, the study was limited for single helium trapping and the mechanism of multi-trapping of helium in a vacancy has not been studied. Recently, Zhang et al. reported the vacancy multi-trapping of helium up to 4 atoms in vanadium by the first-principles [17], but the effect of atomic relaxation was not taken into account. Such a relaxation mode exhibits a large difference on the mechanism of multiple-trapping of helium. In the present work we incorporate the atomic relaxation effect to clarify the detailed picture of helium diffusion, trapping and stability in vanadium.

Despite of these experimental and theoretical studies, many fundamental aspects on the interaction between helium and vanadium are still not fully clear up to now, such as the multi-trapping of helium in a vacancy and the effect of helium on the tensile strength of vanadium. In this paper, the stability, the diffusion of helium, and its interactions with vacancy in vanadium have been studied. Furthermore, we have performed the first-principles computational tensile test (FPCTT) on vanadium with helium. The results will provide a useful reference for vanadium as a structural material in the future fusion reactor.

2. The computational method

Our first-principles calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) code [20,21] based on the density functional theory. The generalized gradient approximation (GGA) of Perdew and Wang [22] and projector augmented wave (PAW) potentials [23] were used in all the calculations. A plane wave energy cutoff of 350 eV was found to be sufficient to converge the total energy and the geometry of bcc vanadium supercell. During the geometry optimization for the bcc vanadium supercell, the Brillouin zone was sampled in terms of the Monkhorst-Pack scheme [24] and the Methfessel–Paxton smearing with a width of 0.20 eV. The calculated equilibrium lattice constant for bcc vanadium was 2.98 Å, in good agreement with the corresponding experimental value of 3.03 Å [25], which demonstrated the accuracy of the current PAW method. For the calculations of the solution energy, the binding energy and the tensile strength, we apply the 128-atom supercell containing $(4 \times 4 \times 4)$ unit cells with the lengths of 11.92 Å in the [101], [010], and [001] directions, respectively. The total energy was found to converge well for the 128-atom supercell with $3 \times 3 \times 3$ *k*-points. During calculations, the supercell size, shape, and atomic positions were relaxed to equilibrium, and the energy relaxation iterates until the forces on all atoms are less than 10^{-3} eV Å^{-1}.

The solution energy of the interstitial helium atom in intrinsic vanadium is defined as

$$E^s_{He} = E_{(n)vanadium,He} - nE_{vanadium} - E_{He}, \tag{1}$$

where $E_{(n)vanadium,He}$ is the energy of the supercell with n vanadium atoms and one helium atom, $E_{vanadium}$ is the energy of an ideal bulk vanadium atom, and E_{He} is the energy of an isolated helium atom.

The binding energy between helium atoms and vacancy for the helium-vacancy complexes (He_nV) is defined by

$$E^b_{He_nV} = [E_{(n)vanadium,He(T-site)} - nE_{vanadium}] - [E_{(n-1)vanadium,He_nV} - E_{(n-1)vanadium,He_{n-1}V}] \tag{2}$$

where $E_{(n-1)vanadium,He_nV}$ and $E_{(n-1)vanadium,He_{n-1}V}$ are the energies of the supercell with He_nV and $He_{n-1}V$ complexes, respectively. $E_{(n)vanadium,He(T-site)}$ is the energy of the supercell with a helium atom at the tetrahedral interstitial site (T-site). Here, negative binding energy indicates repulsion between the helium atom and vacancy, while a positive value indicates attraction.

The trapping energy of helium by vacancy can be usually approximated as the sum of the helium-vacancy binding energy and the migration energy of helium in bulk vanadium, expressed by

$$E^{trap}_{He} = E^b_{He_nV} + E^m_{He}. \tag{3}$$

In the FPCTT, the tensile stress σ is calculated according to the Nielsen-Martin scheme [26] as given by

$$\sigma_{ij} = \frac{1}{\Omega(\varepsilon_{ij})}\frac{\partial E}{\partial \varepsilon_{ij}}, \tag{4}$$

where E is the strain energy and $\Omega(\varepsilon_{ij})$ is the volume at a given tensile strain.

3. Results and discussions

3.1. Energetic stability of helium in bulk vanadium

First, a single helium atom behavior was investigated in bulk vanadium. The solution energies of helium at the T-site (E^s_T) and O-site (E^s_O) are listed in Table 1 in reference to the energy of an isolated helium atom in a large vacuum supercell. In bulk vanadium, E^f_T and E^f_O were calculated to be +3.02 and +3.24 eV, respectively. The results showed that a single helium atom prefers to occupy the T-site and the positive values indicated that the dissolution process of helium in vanadium is endothermic. The relative stability of helium at the T-site and the O-site is consistent with the previous result calculated by Zhang et al. [17]; although the absolute values of helium solution energy are a bit different. However, the effect of ZPE was not considered by Zhang et al. [17] because it should not be neglected for lighter elements in bulk vanadium. The ZPE of helium can be obtained by summing up the zero-point vibrational energies of helium's normal modes, i.e., $(\mathrm{ZPE} = \sum^{h\nu}_{\nu}/2)$, where ν is a real normal mode frequency. The present calculations showed that the ZPEs of helium in vanadium were 0.089 eV and 0.049 eV at the T-site and

Table 1 The calculated ZPE and solution energies (eV) of a helium atom in bulk vanadium.

Configurations	He_{T-site}		He_{O-site}	
ZPE of He	0.089		0.049	
Solution energy				
without ZPE	3.02	2.95 [14]	3.24	3.17 [14]
with ZPE	3.11		3.29	

the O-site, respectively. Table 1 also indicated that the relative stability of helium in the T-site and the O-site remained unchanged, although the ZPE of helium had significant effects on the solution energy of helium.

Recently, a hard-sphere lattice model is shown to represent the effective volume and the stability of interstitial helium in metals [27]. Since helium exhibits a closed shell electronic structure and cannot easily bond with the host metal atoms, it prefers to be bound at a site with larger space and lower electron density in metals. The homogeneous electron gas model [28,29] can also clarify the fact that the helium solution energy will decrease linearly with the decrease in electron density until reaching a minimum $n_0=0$ electron/Å^3. This value reflected that helium would like to occupy the lowest density site, especially the free space. In bulk vanadium, the electron density of the most stable T-site is 0.25 electron/Å^3 is much higher than that of the optimal density of $n_0=0$ electron/Å^3. Thus, it is not favorable for helium to dissolve at the T-site. Furthermore, such higher vanadium atomic density also plays a key role in the interactions of helium with vanadium and can lead to strong short-range repulsion between helium and vanadium ionic cores when helium occupies the interstitial site. Moreover, the higher vanadium atomic density directly leads to the higher electron density. Thus, these reasons can fully explain that the solution energy is higher for helium in the interstitial sites in vanadium.

3.2. *Trapping of helium by a vacancy in vanadium*

Apparently, larger space is needed to decrease the vanadium atomic density so as to decrease the repulsive interaction of ionic cores between helium atoms and vanadium atoms. Moreover, larger space can also decrease the electron density. Naturally, vacancy or void can reduce the atomic and electron density. In order to calculate the helium trapping energy in the vicinity of vacancy, the diffusion energy barrier of helium and the binding energy between helium and vacancy must be determined below.

3.2.1. *Diffusion energy barrier of helium in bulk vanadium*

Far away from the vacancy, helium atom migrates along the interstitial sites. In bcc bulk vanadium metals, helium will diffuse from one T-site to the first nearest neighbor (1NN) T-site via a mediate transition state. The activation energy barrier (E_m) was calculated to be 0.108 eV using the climbing image nudged elastic band (CI-NEB) method [30]. After establishing the diffusion energy barrier of helium, the helium diffusion coefficient can be calculated in vanadium. The helium diffusion coefficient is written as $D = D_0\exp(-E_m/kT)$, where D_0 and E_m are the pre-exponential factor and the activation barrier of helium atom, respectively. For a metal with a cubic structure, $D_0 = n/6((\sqrt{2}/4)a)^2\nu$, where n, a, and ν are geometrical factors for the number of equivalent jump paths ($n=4$ for helium in the T-site), the lattice constant, and the vibration frequency, respectively. The vibration frequency ν of helium can be established in terms of the Werts theory [31]. Finally, the pre-exponential factor D_0 is calculated to be 0.57×10^{-7} m^2/s; in good agreement with the experimental value of 0.40×10^{-7} m^2/s measured by Lewis using the method of the helium ions implantation into the pure vanadium [32].

Moreover, the $h\nu_{H_e}$(0.089 eV in the present calculation) is larger than kT at the room temperature (0.026 eV). The diffusion coefficient is correspondingly expressed as $D = n/6((\sqrt{2}/4)a)^2\ (kT/h)\exp[-(E_m+\Delta ZPE)/kT]$. The exponential term $\Delta E+\Delta ZPE$ can be regarded as a *ZPE*-corrected diffusion energy barrier. Thus, the *ZPE*-corrected activation barrier is obtained to be 0.09 eV, also quantitatively consistent with the experimental result of 0.08 eV [32]. As discussed above, Zhang et al. studied the diffusion of helium in vanadium using the same method as in this work. The helium energy barrier was given to be 0.06 eV, lower than 0.09 eV obtained in the present calculation and 0.08 eV from the experiment. The difference might be due to the difference of the "atomic relaxing mode". During all the calculations, Zhang et al. relaxed all the atomic positions within a constant supercell volume. As plotted in Fig. 1, the helium diffusion coefficient is given as $D_{He} = 0.57\times10^{-7}\exp(-0.09\ \mathrm{eV/kT})\ \mathrm{m}^2/s$. This value can provide a good reference to understand the behavior of helium in bulk vanadium.

3.2.2. *Binding between helium and vacancy in vanadium*

The interaction between helium and vacancy was further investigated. The results showed that the binding energy in vacancy for helium was 1.24 eV, which was larger than ~0.90 eV obtained by Zhang et al. [17]. At the same time, the larger binding energy indicated that it was more favorable for helium to bind with vacancy. Helium is characterized by closed-shell electronic structure, and it prefers to keep such kind of structure energetically. For helium at the interstitial site, there is a very short-range ionic repulsion between helium and vanadium due to the higher vanadium atomic density and core electrons overlap. With the presence of vacancy, the vanadium atomic density can be decreased and can further lead to the weakening of core electrons overlap between helium and vanadium.

One can see that helium and vacancy are strongly bound in vanadium due to the "low atomic and low electron density" region provided by the vacancy; originating the driving force for helium to segregate at the vacancy. Furthermore, the strong binding energy between helium and vacancy indicated that vacancy formation energy can be decreased. This can explain the experimental observation of helium assisting vacancy swelling in some metals [33]. On the other hand, the strong binding of helium with the vacancy demonstrated that vacancy might provide binding centers which drive large amount of helium atoms to segregate into the vacancy.

Helium atoms were sequentially put into the vacancy and the binding energies of other helium atoms with the vacancy were also calculated, as illustrated in Fig. 2. For the interactions of double helium atoms with vacancy, the He_2V complex is denoted. It is formed by $He_1V+He\rightarrow He_2V$. Here, the <100>, <110>, and <111> symmetrical dumbbell configurations were only

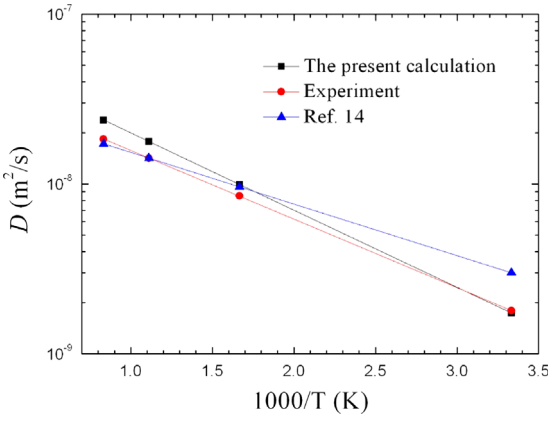

Fig. 1 Diffusion coefficients of helium in vanadium via interstitial mechanism as a function of reciprocal temperature.

considered. The binding energies between the second helium atom and He_1V for the three different cases are summarized in Table 2. It is important to note that the <111> dumbbell for He_2V is more favorable with a binding energy of 1.96 eV in comparison with the <110> and <001> dumbbells with the respective binding energy of 0.81 eV and 0.77 eV.

Encouraged by the results of strong binding between double helium atom and vacancy, helium atoms were placed continuously into vacancies with numbers 3, 4, 5, and 6. As shown in Fig. 2, the binding energy (0.59 eV) suddenly became lower in comparison with the second one (1.96 eV) when the third helium atom was placed into the vacancy. This indicated that the formation of the He_3V complex induced an energy release of 0.59 eV. With the increase of helium number up to six, the energy release increased again. The formation of He_4V from He_3V+He can induce an energy release of 0.99 eV, and the formations of He_5V from He_4V+He and He_6V from He_5V+He are also exothermic with the respective energies release of 1.29 eV and 1.34 eV. Therefore, the vacancy can provide a lower atomic and electron density which could lead to helium segregation into the vacancy and thus the helium aggregation in vanadium.

It should be noted that the relaxation procedure can affect the calculated accuracy of the binding energies for the He_nV complexes. We compared the binding energies of $He_nV = He + He_{n-1}V$ between the present calculations and the results calculated by Zhang et al. [14], using the same method and nearly the same parameters as in this work such as the PAW potentials and the energy cutoff of 350 eV; but the only difference was whether the supercell was relaxed or not. As shown in Fig. 2, the binding energies are quite different between the two ways from 1 to 3 helium atoms, but are basically in accordance with each other from 4 helium atoms onwards, demonstrating the effects of different relaxation methods on the calculated binding energies of helium.

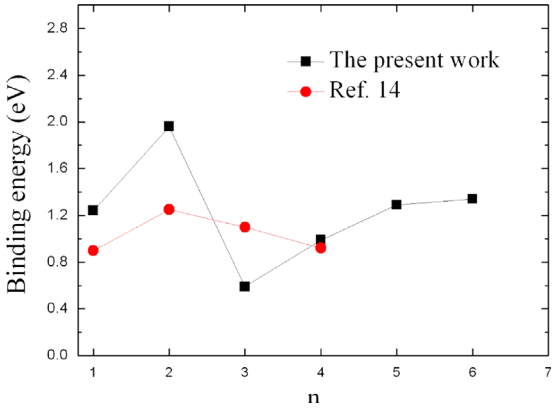

Fig. 2 The binding energy of helium with He_nV at vacancy in vanadium. The energy zero-point is the energy of helium in the T-site far away from the vacancy.

Table 2 The binding energy (eV) of the second helium atom with He_1V and He–He equilibrium distance (Å) using a 128-atom supercell.

Configuration	Binding energy	He–He equilibrium distance
<001>	0.77	1.90
<110>	0.81	1.68
<111>	1.96	1.49

The helium trapping energy as a function of the number of helium atoms is shown in Fig. 3. Far away from the vacancy, the helium atom diffuses along the interstitial sites with an energy barrier of 0.09 eV. However, the helium atom will undergo a diffusion process with downgrade of energy towards the vacancy center after it diffuses near the vacancy. Moreover, if helium atom diffuses into the vacancy, it has to overcome a large de-trapping energy to recur to the bulk interstitial sites.

As a result, a vacancy can lead to direct helium segregation towards it and it easily traps helium atoms by providing the "lower atomic and electron density region" as a large driving force for the helium binding. For the multi-vacancy case, it can be naturally deduced that vacancies and voids with much lower atomic and electron density region can trap more helium atoms to form larger helium blistering. For instance, the stabilities of He_nV complexes have been investigated systematically in other metals such as iron and tungsten [33–35]. Since helium prefers to occupy the low-eratomic and electron density region that the defect-free vanadium cannot provide, helium may spontaneously enhance the formation of vacancy-like defects to decrease the atomic and electron density in vanadium or other metals so as to make itself comfortable.

3.3. *The effect of helium on ideal tensile strength of vanadium*

As investigated above, helium atoms have a strong tendency to aggregate, and thus form bubble quite easily in the vicinity of vacancy. Even helium with low concentration case is also expected to have great effects on the mechanical properties of vanadium such as the tensile strength. In order to attest this point, the FPCTTs were performed on two types of pure vanadium and helium-vanadium system cases.

Fig. 4 showed the stress as a function of tensile strain. For pure vanadium case, the stress increases with the increasing strain until it reaches a maximum of 19.1 GPa at a strain of 18%, beyond this point the stress decreases. Thus, the ideal tensile strength is 19.1 GPa in the [001] direction. While when one helium atom is present in vanadium, the stress reaches a maximum of 14.1 GPa at the strain of 14%. The tensile strength and the strain decrease by 26% and 22% in the [100] direction, respectively. This demonstrates that helium obviously affects the tensile strength of vanadium. With the increasing number of helium atoms in vanadium, the tensile strength will be further reduced.

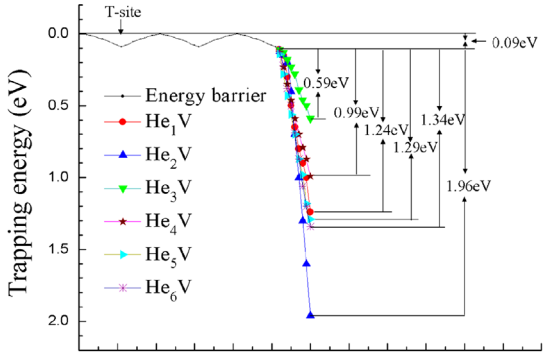

Fig. 3 The helium trapping energy at vacancy in vanadium. The energy zero-point is the energy of helium in the T-site far away from the vacancy.

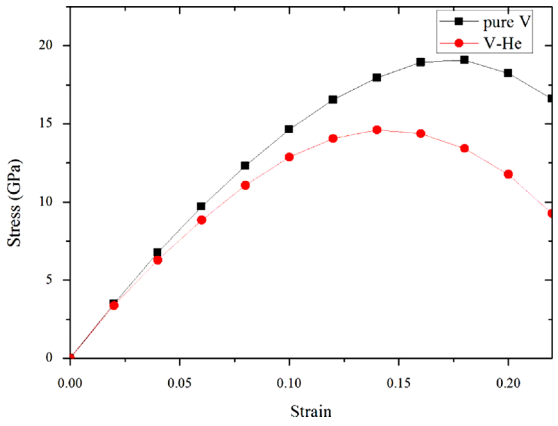

Fig. 4 Stress as a function of strain under tension in the [001] direction for vanadium with and without helium.

4. Conclusions

Using the first-principles calculations, the helium behaviors in vanadium including the stability, its interactions with vacancy and the ideal tensile strength have been investigated. The helium diffusion energy barrier is 0.09 eV, quantitatively consistent with the experiment result of 0.08 eV. Helium atoms are easily trapped by vacancy to form He_nV complexes with large binding energies by providing the "lower atomic and electron density region" as a large driving force for helium binding. The first-principles computational tensile test (FPCTT) demonstrated that the tensile strength can be decreased by 26% in the [100] direction due to the presence of helium in comparison with the pure vanadium case. These results will provide a useful reference for vanadium as a structural material in the future fusion reactor.

Acknowledgments

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